A Quantitative Method for the Evaluation of Silica Flux used in Copper Smelting

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ABSTRACT

In the smelting of copper and copper/nickel concentrates or mattes, the role of silica flux is to aid in the removal of iron by forming a slag phase. Alternatively, the role of flux may be regarded as a means of controlling the formation of magnetite, which can severely hinder the operation of a furnace. To adequately control the magnetite level, the flux must react rapidly with all of the FeO within the bath. Currently flux materials are chosen based on their silica content and on the knowledge of the furnace operators. This disregards both the melting point and the free silica content of the flux, two important flux characteristics. The aim is to develop a rapid method for silica flux evaluation that can be used directly within the smelter.

Samples of flux were mixed with iron sulphide and magnetite and then smelted at 1250°C. Argon was used as a carrier gas for any gaseous products and was analyzed continuously for sulphur dioxide. Thermodynamics indicate that this is the predominant sulphur product. The resulting plot of sulphur dioxide concentration with time was found to contain two peaks, the first one being independent of the flux content of the sample. A flux quality parameter has been defined as the height to time ratio of the second peak. The value of this parameter for pure silica is 5094 ppm/min.

The effect of silica content, silica particle size and silicate mineralogy were investigated using the test apparatus. It was found that a limiting flux quality is achieved at particle sizes less than 0.1 mm in diameter and that feldspar containing fluxes are generally of a poorer quality. The relative importance of free silica and melting point were also studied using synthetic flux mixtures, with free silica displaying the strongest effect.

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Une Méthode Quantative Pour Évaluer le Flux au Silice Employé dans le Fondant du Cuivre

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ABSTRACT

Quand on fond les concentrés ou les mattes au cuivre ou au cuivre/nickel, le rôle du flux au silice est d'aider à éliminer le fer par faire une phase de scorie. Alternativement, le rôle du flux peut être consideré car une méthode à contrôler la formation de Fe_3O_4, qui peut empêcher l'operation du fondeur. Pour suffisamment contrôler la concentration de Fe_3O_4, le flux doit réagir rapidement avec tout le FeO dans le bain. Maintenant, on choit les matériaux du flux car leurs contenus du silice et sur la connaissance des opérateurs. Ce procès néglige la température à fondant et la concentration du silice libre, qui sont deux importants caractéristiques du flux. Le but est à développer une méthode rapide à évaluer le flux au silice qu'on peut utiliser directement dans le fondeur.

Des échantillons du flux étaient mélangé avec FeS et Fe_3O_4, puis fondu à 1250°C. On avait utilisé l'argon pour un gaz portant pour quelques produits gazeux. Le gaz était analysé continuellement pour SO_2. Les thermodynamiques indiquent que ça c'ést le produit du soufre prédominant. Le graphique de la concentration de SO_2 contre le temps contient deux sommets; le premier est indépendent de la quantité du flux dans l'échantillons. Un indice de la qualité du flux était défini puisque le rapport de l'hauteur à temps de deuxième sommet. La valeur de cet indice pour le silice pur est 5094 ppm/min.

Les effets de la concentration du silice, la grandeur des particules au silice et la minéralogie étaient recherché par utilisant l'appareil d'essai. On a trouvé qu'il y a une limite de la qualité du flux aux particules aux diamètres aux moins de 0.1 mm. Aussi, les flux qui contient le feldspar sont de la pauvre qualité. Les importances relatifs du silice libre et la température à fondant étaient étudié par utilisant les mélanges du flux synthétiques. Le silice libre a exhibé l'effet le plus fort.

I. INTRODUCTION

In the smelting of copper and copper/nickel mattes, it is widely accepted that the role of silica flux is to aid in the removal of iron. This is accomplished by a reaction between the silica (SiO_2) in the flux and the wustite (FeO) that results from oxidation of the concentrate or matte. A slag phase comprised of fayalite (Fe_2SiO_4) is formed and can be tapped or skimmed from the surface of the matte by virtue of its density difference.

Alternatively, the role of silica flux can be depicted as a means of controlling the level of magnetite (Fe_3O_4) within the furnace. Because magnetite can be detrimental as well as beneficial to the operation of copper smelting vessels, control over its rate of formation and dissolution is advantageous. As many furnaces are pushed far beyond their designed production rates, the rates of magnetite dissolution and slag formation become even more important.

The behaviour of magnetite in copper smelting vessels has been well documented by several investigators[1-5], although the behaviour of magnetite in copper converters has received much less attention.[6] Kinetic studies on the dissolution of magnetite in Fe-S-O mattes have been carried out by Kaiura and Toguri[7] as well as Asaki *et al.*[8]

The physical chemistry of copper smelting slags has been studied and reported by numerous investigators such as Biswas and Davenport[6] and Elliott[9]. The areas that have been overlooked are the thermodynamics and kinetics of slag formation. Although Asaki *et al*[10] have reported on a kinetic study of the reaction between solid silica and molten matte, no attempts have been made to quantify the effectiveness of silica fluxes. Thus, a greater understanding is required of how flux characteristics (chemical, mineralogical and physical) enhance the slag reaction.

As a means of quantifying the effectiveness of silica flux mixtures, a standardized test will be developed. The test must meet the requirements of being quick, simple to perform and the results must be easy to interpret and consistently reproducible. Meeting these criteria will make the test useful directly within the smelter. It is intended that the test be used to inform operators of daily fluctuations in flux quality, in addition to its use as an experimental tool for testing potential flux mixtures.

II. EXPERIMENTAL

A. Sample Preparation

Samples were prepared by mixing 0.118 g of FeS and 1.18 g of Fe_3O_4 with an appropriate amount of flux ground to the correct particle size. Using the silica assay of the flux, the mass of flux that contains 0.50 g of SiO_2 was calculated and added to the sample. These reactant quantities correspond to 21% excess magnetite and 20% excess silica. A standard sample was made up using pure quartz as the fluxing agent. All three reactants were mixed intimately before placing the sample in a fireclay boat, with dimensions as shown in Figure 3. A ceramic cover that is open at both ends was placed over the sample to prevent splattering within the furnace and at the same time allow the escape of gases. The reactants used were laboratory grade and ground to a fine powder.

B. Apparatus and Procedure

The testing procedure that has been developed is based on the chemistry of the slag forming reactions. Asaki *et al*[8] and various authors agree that slag is produced by two reactions occurring in series. (equations 1 and 2)

$$FeS + 3\ Fe_3O_4 = 10\ FeO + SO2\ (g) \qquad (1)$$

$$2\ FeO + SiO_2 = Fe_2SiO_4 \qquad (2)$$

Kaiura and Toguri[7] have reported that the kinetics of reaction (1) are quite fast. The results of this work confirm their conclusion, and indicate that the kinetics of reaction (2) are significantly slower. Assuming that the system becomes saturated with FeO relatively quickly, the progress of reaction (2) can be monitored by measuring the rate of evolution of sulphur dioxide produced in reaction (1).

The testing apparatus was designed to meet the following requirements: continuous removal and analysis of the reaction offgas, quick insertion of the sample and sealing of the furnace, quick heating of the sample and accurate control of the sample temperature.

The central component of the apparatus is a silicon carbide rod resistance furnace with a mullite combustion tube. The arrangement of the heating rods around the mullite tube is shown in Figure 1. Argon is used as a carrier gas for the evolved sulphur dioxide evolved and its flowrate is measured and maintained with the use of a rotameter. The furnace offgas is passed through glass wool to remove any particulate matter before entering an infrared sulphur dioxide analyzer. The analyzer signal is transmitted to a chart recorder to generate a continuous plot of sulphur dioxide concentration. The arrangement of the equipment is illustrated in Figure 2.

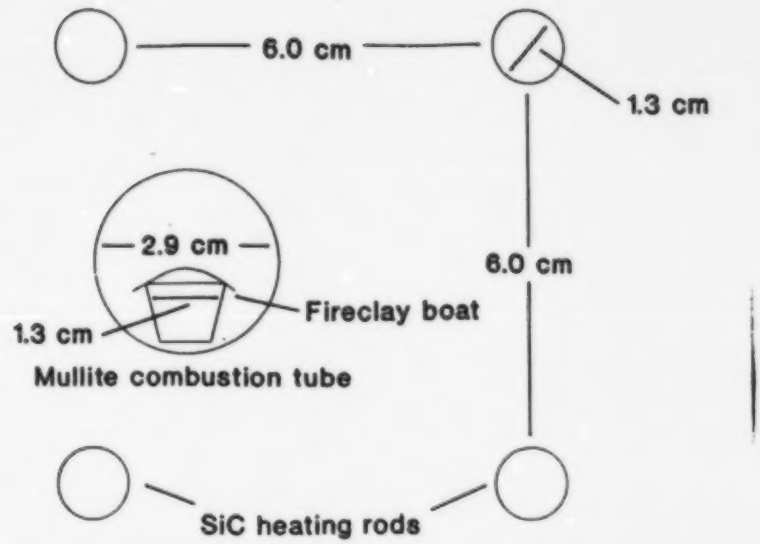


Figure 1 - Arrangement of Heating Elements

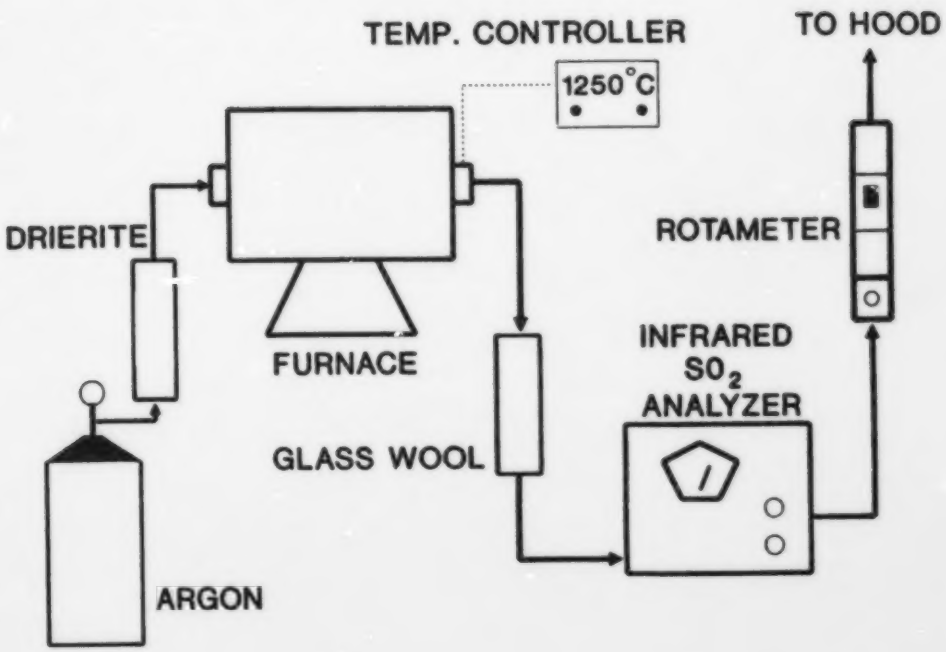


Figure 2 - Test Apparatus and Gas Train

One end of the combustion tube has a removable cap that provides easy access to the reaction zone. The sample is placed into the tube counter-current to the flow of argon to minimize entrainment of oxygen within the furnace. The end cap also holds a thermocouple in place for measuring the furnace temperature. The position of the sample crucible within the mullite tube is shown in Figure 3.

The sample was smelted at 1250°C, a temperature most typical of current smelting operations.[11] The furnace temperature controller was operated in on/off mode as this was found to provide the fastest heating with an acceptable fluctuation around the target temperature. The furnace temperature oscillated within ±4°C after reaching the setpoint. The temperature of a sample of powdered Al_2O_3, with thermal mass equal to that of a standard sample containing quartz flux is shown in Figure 4. The temperature was measured from the instant that the sample was placed in the furnace with the thermocouple tip in direct contact with the sample. Although a slight temperature gradient exists along the axis of the tube, this is negligible in the vicinity of the sample.

The variables that were isolated and investigated independently are: presence of silica, carrier gas flowrate, percent of the stoichiometric silica requirement, silica particle size, sample preparation technique and flux silicate mineralogy. The technique used for sample preparation was studied by compacting the sample into cylindrical discs under various pressures.

The investigation into the effect of silicate mineralogy was carried out as a two-part study. Initially a variety of current fluxing materials were obtained from three different smelting operations within Ontario. After being analyzed for mineral content by x-ray diffraction and chemical content by x-ray fluorescence spectroscopy, these fluxes were ground to a common particle size and then tested for flux quality. The results of the mineral and chemical analysis may be referred to in Tables I and II respectively.

Secondly a number of simple silicate minerals were prepared synthetically in the following manner: The stoichiometric amount of each metal oxide in the silicate mineral was mixed together and then pressed into a cylindrical disk under a pressure of 8000 psi. The disks were then sintered at 1200°C in an air atmosphere. Some samples were sintered at a slightly lower temperature to avoid melting. After 24 hours of sintering the samples were analyzed by x-ray diffraction for residual free silica. Samples that still exhibited a significant silica content were sintered for an additional 24 hours and then retested. The list of simulated flux mixtures that were prepared is found in Table III.

To determine the effect of non-silicate minerals present in the flux, two synthetic flux mixtures were prepared by mixing the required amount of silica with varying

amounts of alumina.

The procedure for carrying out the flux test was as follows: After each sample was prepared and the furnace had reached the operating temperature, the carrier gas flowrate was set to 2.0 L/min. The basis for choosing this flowrate is explained later in this report. The sample was then inserted into the furnace and the end cap was sealed immediately. Analysis of the offgas was continued until the sulphur dioxide concentration had effectively reached zero, a duration of 5 to 10 minutes depending on the quality of the flux. Upon completion of the test the crucible was removed from the furnace and the apparatus was ready to accept another sample.

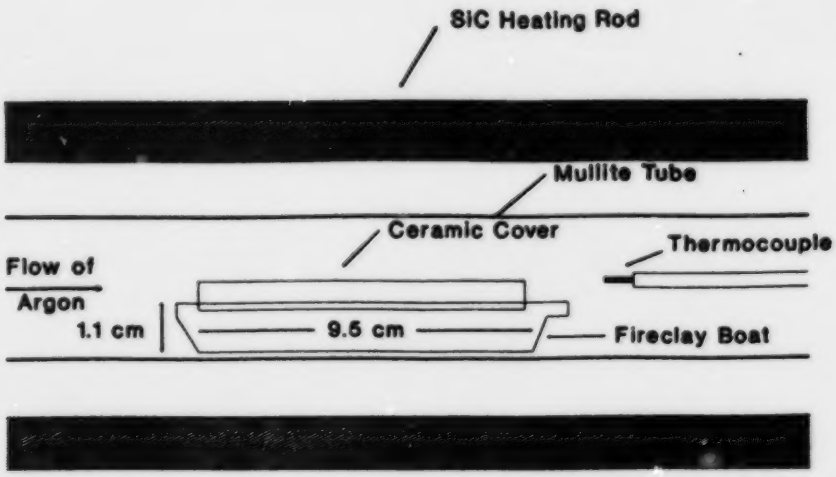


Figure 3 - Arrangement of Crucible within Furnace

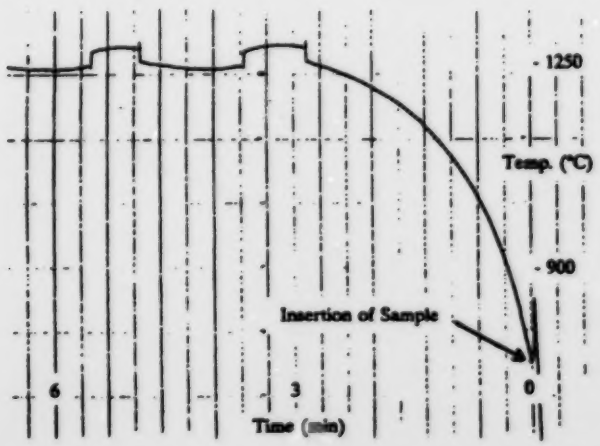


Figure 4 - Thermal Response of Powdered Alumina Sample

Table I - X-ray Diffraction Analysis of Industrial Fluxes and Flux Quality Results

Flux I.D.	Mineralogy	% Silica	FQP (ppm/min)
101	Major quartz. Minor feldspar. Trace calcite, chlorite, dolomite, amphibole.	78.9	4036
102	Major quartz.	99.0	4902
103	Major quartz. Minor feldspar, chlorite, dolomite. Trace calcite, mica.	58.4	3328
104	Major quartz. Minor mica, calcite. Trace chlorite, feldspar.	79.6	4599
201	Major quartz. Trace chlorite, mica.	96.5	4524
202	Major quartz. Minor feldspar (albite and microcline). Trace dolomite.	80.6	3681
301	Major quartz. Minor chlorite, mica, feldspar. Trace calcite.	78.6	3399
302	Major quartz. Minor feldspar. Trace chlorite, mica, calcite.	83.5	3837
401	Major quartz.	100.0	5094
501	Major quartz. Minor feldspar. Trace chlorite, amphibole.	79.9	3696

Table II - X-ray Fluorescence Spectroscopy Analysis of Industrial Fluxes

Flux ID	101	102	103	104	201	202	301	302	501
SiO2	78.9	99.0	58.4	79.6	96.5	80.6	78.6	83.5	79.9
Al2O3	11.4	0.41	13.1	8.48	1.26	9.89	10.7	8.33	8.01
CaO	2.50	0	5.59	1.50	0	2.14	1.11	1.21	1.45
Na2O	1.78	0.09	1.19	0.69	0	1.39	1.59	1.22	2.21
K2O	1.89	0	1.27	2.16	0.10	1.52	1.72	1.44	1.64
MgO	0.62	0	3.47	0.93	0	0.73	1.15	0.80	0.86
FeO	1.44	0.14	7.91	4.41	2.05	1.45	3.48	2.23	1.8
S	0.02	0.01	2.11	1.81	0.01	0.05	0.02	0.01	na
Totals	98.6	99.7	93.0	99.6	99.9	97.8	98.4	98.7	95.9

III. RESULTS

The experiments clearly show that the test results differ greatly when quartz is added to a sample containing only iron sulphide and magnetite. Figure 5 contrasts the results obtained for no flux and pure silica flux. It appears that the first peak obtained in the plot of sulphur dioxide concentration with time is independent of the flux content of the sample. The second peak however, does appear to be greatly influenced by the presence of flux.

As a means of quantifying this effect, we have devised the following parameter as an indication of the flux quality:

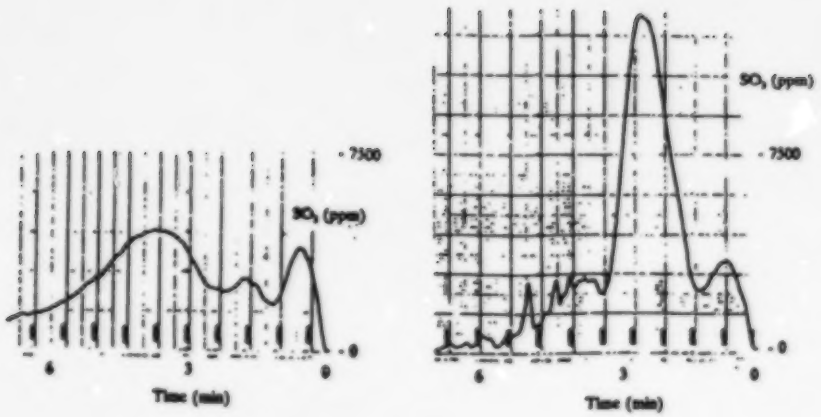
$$\textit{Flux Quality Parameter} = \frac{\text{height of second peak}}{\text{time to reach second peak}} \qquad (3)$$

By using the height to time ratio for the second peak, this parameter incorporates both the speed of the reaction as well as the extent of the reaction. The value of the FQP for pure silica flux has been found to be 5094 ppm/min and for a sample containing no flux the experimental value is 1300 ppm/min.

The results of varying the amount of silica present in the sample are shown in Figure 6. The flux quality increases in a nearly linear fashion with increasing silica content but then reaches a limiting value when 60% of the stoichiometric silica requirement is present. This limiting value is maintained up to 20% excess silica.

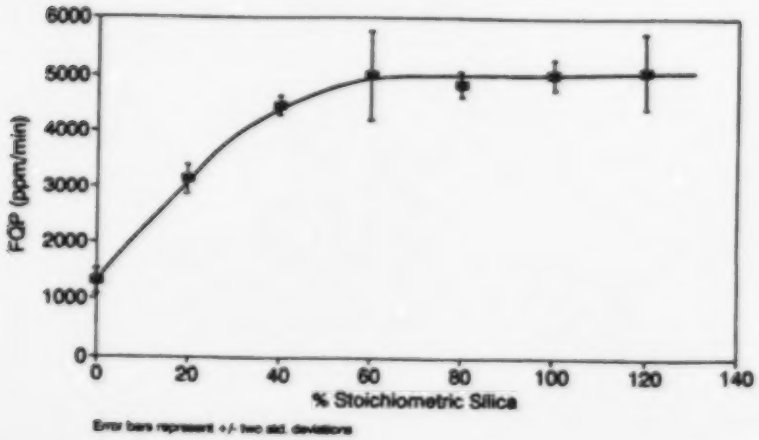
Figure 7 illustrates the effect of silica particle size on the flux quality parameter. The flux quality parameter has been plotted against surface area since the slag reaction is believed to occur at least in part at the surface of the silica particle.[10] A semi-logarithmic scale was used to accommodate a wide range of particle sizes. The flux used in these experiments is #102. X-ray fluorescence spectroscopy showed that this flux contains over 99% silica, and can be considered to be pure quartz. This was confirmed by x-ray diffraction analysis. The flux quality increases with decreasing particle size but reaches both upper and lower limiting values. The upper value is observed for particle diameters less than 0.1 mm and the lower limit occurs at a particle diameter of 4.0 mm.

To insure that the carrier gas flowrate is sufficiently high to prevent gas phase diffusion resistance, the argon flowrate was varied from 1.2 L/min to 4.0 L/min. A flux quality parameter that should be independent of gas flowrate was then calculated and plotted in Figure 8. To normalize the flux quality parameter with respect to gas flowrate, the FQP was multiplied by the argon flowrate (resulting units are moles SO_2/min^2). The



a) No flux b) Pure quartz flux

Figure 5 - Test results for a) no flux and b) pure quartz flux



Error bars represent +/- two std. deviations

Figure 6 - Variation of FQP with Sample Silica Content

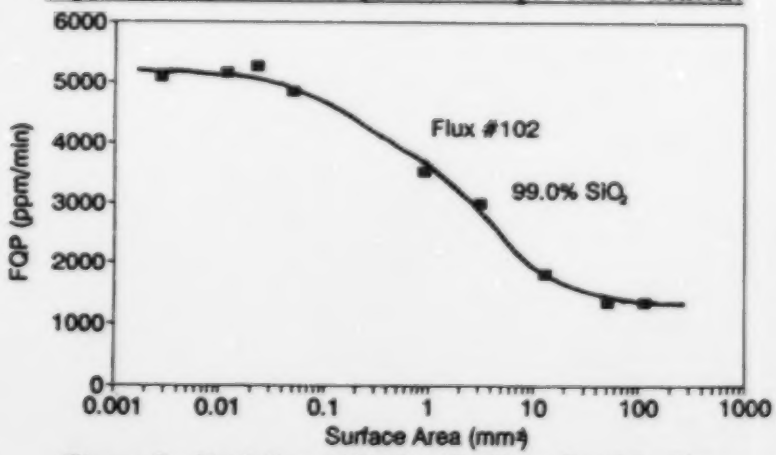


Figure 7 - Variation of FQP with Silica Particle Size

plot indicates that this normalized parameter is constant at carrier gas flowrates above 2.0 L/min.

The effect of pressing the sample into a cylindrical disk is shown in Figure 9. This figure contrasts the test results obtained for pure silica flux. The sample in Fig. 9b) has been prepared as a loose powder in the standard manner while the sample in Fig. 9a) has been compacted under a pressure of 8000 psi. The disk had a diameter of 11 mm and a thickness of 5 mm. Although the second peak is achieved more quickly in Fig. 9a), virtually on top of the first peak, it is much broader than that of Fig 9b). It is also important to note that the small peaks that appear near the end of the test are accentuated by the compacting procedure.

Figure 10 is a plot of the FQP as it varies with the compacting pressure used in forming the samples into disks. The flux quality parameter is generally less than that obtained for a sample prepared in the standard manner and the curve exhibits a slight maximum at a pressure of 2000 psi.

The investigation into the effect of silicate mineralogy is considered the most important and therefore it receives the greatest attention. Figure 11 is a plot of FQP versus silica content for the industrial flux mixtures. The purpose of this graph is to illustrate that there is a very weak correlation between the flux quality and the silica assay of the flux. Also located on this graph are the two flux mixtures containing only silica and alumina.

To gain an understanding of which minerals enhance or diminish the flux quality, the same points have been replotted in Figure 12 in descending order. The inset table on this graph lists the minor minerals present in each flux. The single major mineral present in each flux was quartz. As reference points, the test results for both pure silica and no flux have been included.

Figure 13 shows the variation of the FQP for the synthetic flux minerals. These have also been arranged in decreasing order of flux quality, to identify the best silicate minerals for fluxing. By referring to this graph and the data listed in Table IV, some conclusions can be made regarding the relative importance of melting point and free silica with respect to flux quality. The second last column of Table III contains the free energies of the reactions by which slag is formed from the silicate minerals listed, producing fayalite and the remaining metal oxide. A general reaction of this type is given below the table. The free energies were evaluated using the CSIRO-MONASH Thermochemistry System Program version 5.1 © 1990.

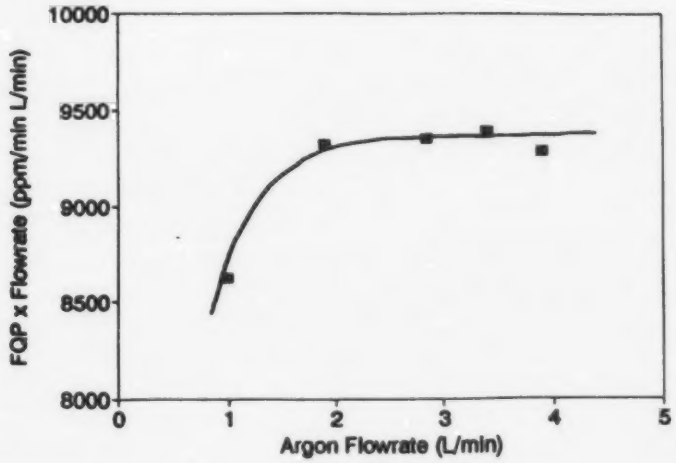
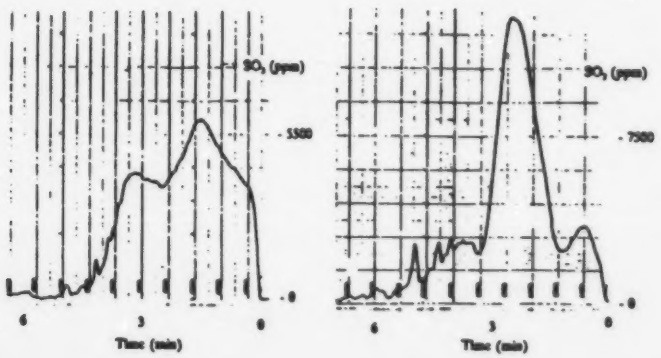


Figure 8 - Variation of Normalized FQP with Carrier Gas Flowrate



a) Pelletized at 8000 psi b) Loose powder

Figure 9 - Test results for samples prepared as a a) cylindrical disc and b) loose powder

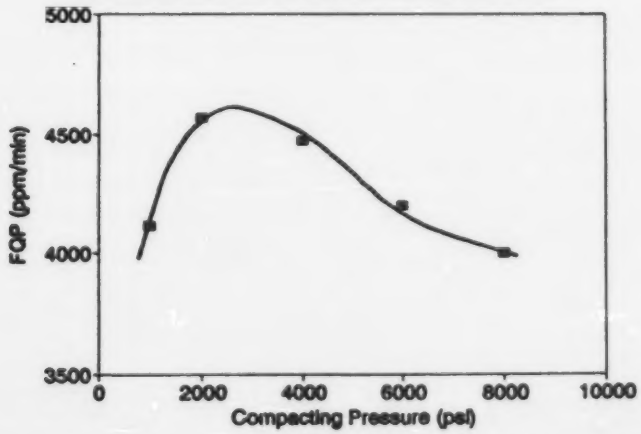


Figure 10 - Variation of FQP with Compacting Pressure

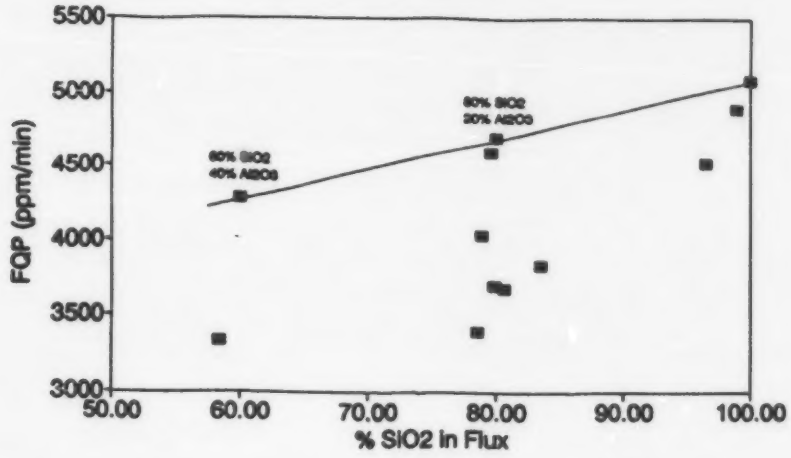


Figure 11 - Variation of FQP with Silica Content of Industrial Fluxes

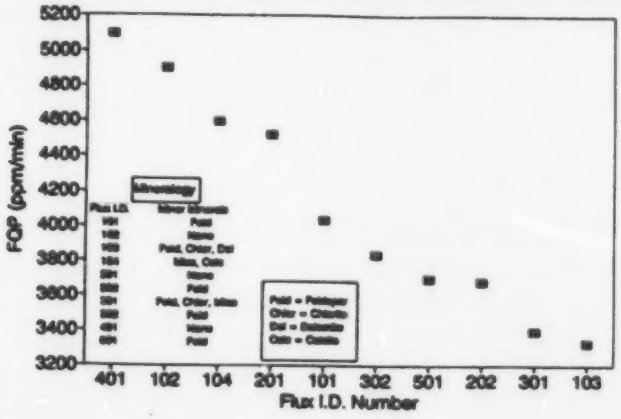


Figure 12 - Variation of FQP with Mineralogy : Effect of Minor Minerals

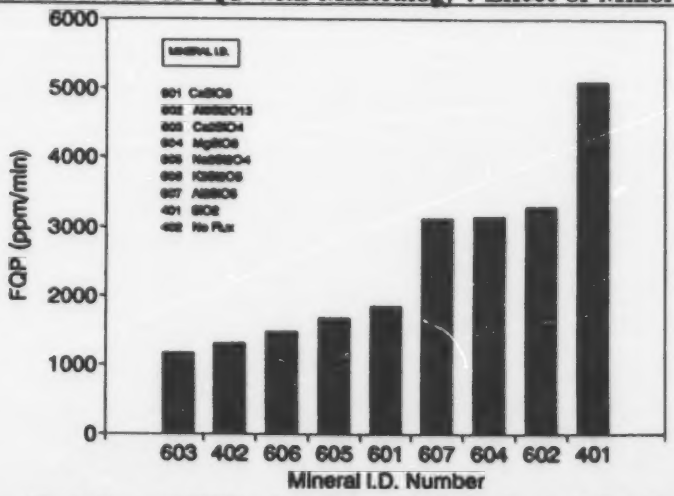


Figure 13 - Variation of FQP with Silicate Mineralogy of Synthetic Fluxes

Table III - Melting Point vs. Free Silica of Synthetic Flux Compounds

Mineral ID	Formula	% Silica	Melting Pt. (°C)	ΔG_r ->Slag (kJ/mol)*	FQP (ppm/min)
601	CaSiO3	51.7	1540	+62.1	1853
602	Al6Si2O13	28.2	1850	-12.6	3294
603	Ca2SiO4	34.9	2130	+106.9	1170
604	MgSiO3	59.9	1577	+2.95	3146
605	Na2Si2O5	66.0	875	+97.5	1682
606	K2Si2O5	56.1	1045	+144.6	1473
607	Al2SiO5	37.1	1600	-20.8	3127
401	SiO2	100.0	1720	-28.0	5094

* Slag Reaction is: $M_xO_y \cdot SiO_2 + FeO = Fe_2SiO_4 + M_xO_y$ (at 1250°C)

where M_xO_y represents a metal oxide from period I or II.

Table IV - Chemical Structure of Minerals Present in Industrial Fluxes

Mineral/Group Name	Chemical Formula
Quartz	SiO_2
Feldspar (group)	Silicates of Al with Ba, K, Na or Ca. Most common: Orthoclase $KAlSi_3O_8$ Group formula: $(Na,Ba,K,Ca)AlSi_3O_8$
Albite (a Feldspar)	$NaAlSi_3O_8$
Microcline (a Feldspar)	$KAlSi_3O_8$
Chlorite (group)	Silicates of Al with Fe(2+), Mg and H_2O. Group formula: $(Mg,Fe)_2Al_2SiO_7 \cdot 2H_2O$
Amphibole (group)	Silicates of Fe, Mg, Mn, and Ca. Group formula: $(Fe,Mg,Mn,Ca)SiO_3$
Mica (group)	Silicates of Al with K and H. May also contain Mg, Fe(2+), Fe(3+), Na or Li. Most common: Muscovite $H_2KAl(SiO_4)_3$
Calcite *	$CaCO_3$
Dolomite *	$CaMg(CO_3)_2$

* not silica containing minerals.

IV. DISCUSSION

In reference to Figure 4, the sample reaches the required temperature of 1250°C very rapidly. This temperature is achieved in less than 3 minutes, after which the furnace cycles on and off maintaining a temperature between 1246°C and 1254°C. A slight shift in the temperature scale is noticed when the furnace turns on or off due to electrical noise.

The test results for pure silica flux (#401) and no flux (#402) presented in Figure 5 clearly show the similarity between the first peaks and the difference between the second peaks in the test output. The first peak may be explained by the sample becoming saturated with FeO very quickly as a result of the reaction between FeS and magnetite (1). As the reaction between FeO and silica (2) begins to take place, the activity of FeO in the melt is lowered, allowing reaction (1) to proceed further to the right. Since the kinetics of (1) appear to be much quicker than those of (2), the progress of reaction (2) can be followed by monitoring the evolution of SO_2 in reaction (1). The small peaks that appear in the tail of Figure 5b are likely due to the high viscosity of the sample resulting in gases being released as bubbles. At this point in the test, the sample contains primarily a fayalite slag that is saturated in both silica and magnetite.

It may be expected that the graph in Figure 5a would only contain one peak since there is no flux present to support reaction (2). The second peak that occurs is likely due to the heating of the sample that takes place in the first few minutes of the test. Since reaction (1) is endothermic[12], as the temperature increases the equilibrium constant increases as well. This shift to the right in the equilibrium results in a gradual evolution of SO_2, as evidenced by the second peak.

Figure 6 shows the variation of the flux quality parameter with the silica content of the sample. The ultimate value of the FQP for pure silica is achieved in samples containing approximately 60% of the stoichiometric silica requirement. This indicates that the flux is responsible for about 60% of the sulphur dioxide produced during the experiment. The remaining 40% can be attributed to the equilibrium of reaction (1), which is observed when no flux is present. Since the FQP is not affected by silica additions up to 20% excess of the stoichiometric requirement, silica saturation can be maintained throughout the test without altering the results.

The plot of flux quality parameter against silica particle surface area in Figure 7 shows that the FQP is independent of particle size in two regimes. The limiting value that occurs for particle diameters greater than 4 mm may not be a true minimum but

rather may be due to the size of the crucible. At this point the flux particle diameter is approaching the width of the sample boat. The limiting value that occurs for particle diameters less than 0.1 mm does appear to be a true maximum. Assuming that the reaction is controlled primarily by diffusion and reaction kinetic limitations, it is at this particle size that the diffusional resistance becomes negligible and the reaction is controlled entirely by kinetics. Since kinetics are independent of particle size, the flux quality parameter becomes independent of particle surface area. It is for this reason that all other experiments were carried out using flux ground to a particle size of 0.1 mm.

Figure 8 illustrates that the flux quality parameter is independent of carrier gas flowrate at argon flowrates of 1.9 L/min and greater. At flowrates lower than 1.9 L/min, the value of the normalized value of the FQP decreases. This is likely due to gas phase resistance that broadens the SO_2 concentration curve. The testwork was carried out with a carrier gas flowrate of 2 L/min to eliminate this effect.

The experimental results for pure silica, prepared both as a loose powder and as a disk compacted at 8000 psi are shown in Figure 9. In Figure 9a, the first peak is barely distinguishable from the second, but it still appears to be at the same height (3700 ppm). It was speculated that the first peak may be due to a reaction between iron sulphide in the sample and oxygen that was present either in the void space of the sample or at the surface of the sample. Compacting the sample should reduce the amount of oxygen present at both of these locations. Since the height of the first peak was unaffected by compacting the sample under various pressures, this theory was rejected.

Compaction of the sample resulted in a greater amount of SO_2 being released after the second peak, likely due to greater resistance mass transfer from the sample into the bulk gas phase. Based on this result, the best method for performing the flux test is to use samples prepared as a loose powder.

Figure 10 illustrates the effect of compacting samples containing pure silica under various pressures. The optimum pressure of 2000 psi results in a flux quality parameter of 4600 ppm/min. Below this pressure there is poorer contact between the reactants, resulting in a slower and broader peak. At pressures higher than 2000 psi, the disk thickness was constant, indicating the same degree of contact between the reactants. Thus, the higher pressures only serve to increase the resistance to gas transfer out of the sample.

The purpose of Figure 11 is to illustrate that there is a weak correlation between flux quality and the silica assay of the flux. As expected, the general trend is that higher flux quality is achieved with fluxes containing fewer impurities, but it is not possible to

predict the flux quality based solely on the silica assay. This is because the assay does not provide any information regarding the mineralogy of the flux.

The results of the FQP evaluation for samples containing silica with varying amounts of alumina form a straight line that passes through the result for pure silica. Alumina was chosen as the additive since it is the second most abundant component in all of the industrial fluxes (see Table II). Although this line appears to form an upper limit on the flux quality, further experimentation is required to confirm this result.

The data in Figure 11 has been plotted in descending order in Figure 12 with mineralogical information. The best fluxes were found to be those containing no minor minerals as well as a flux containing both mica and calcite. As expected, calcite does not significantly affect the flux quality since it is silica free. However, it is interesting that mica does not result in a poor flux quality either, since it does contain silica. The chemistry of all the minerals present in the industrial fluxes can be referred to in Table IV.

Flux mixtures containing feldspar exhibit a poorer quality than those without feldspar. This indicates that some of the silica contained in feldspar minerals is not free silica (available for fluxing). Differences between fluxes containing the same minor minerals are due to varying amounts of these minerals and the presence of trace minerals. Table I lists the complete mineral analysis of these fluxes. When feldspar is combined with either chlorite and mica or chlorite and dolomite, the flux quality is even poorer. This indicates that chlorites are also detrimental to flux quality.

The results for the synthetic flux mixtures are shown in Figure 13. Both of the alumina-silicates and the magnesia-silicate exhibit the best flux quality of the minerals tested, but still much lower than pure silica. It appears that these minerals do contain free silica, but the kinetics during the release of this silica cannot be ignored. The thermodynamic results presented in Table III show some support for this observation. These flux minerals melt at approximately the same temperature as pure silica, thus melting point is not a factor.

The other minerals tested show very poor flux quality, marginally better than the results obtained for no flux. These results are in good agreement with the thermodynamic analysis. Two of the minerals in this group melt at temperatures much lower than 1250°C, demonstrating that melting point does not have a strong effect on the flux quality. The flux containing dicalcium-silicate displayed an even poorer flux quality than samples containing no flux at all. This is possibly due to its extremely high melting point (2130°C).

V. CONCLUSIONS

A high temperature resistance furnace connected to a Lira® infrared gas analyzer was used to develop a method for quantifying the effectiveness of silica flux mixtures. The test was designed to be quick, providing results that are reproducible and easy to interpret. The flux reaction was monitored indirectly by measuring the evolution of sulphur dioxide. Analysis of the results provides an evaluation on both a kinetic and a thermodynamic basis.

The following conclusions can be made as a result of this work:

1) The equilibrium between FeS/Fe_3O_4 and FeO/SO_2 is established very quickly and is responsible for the first peak in the test output. This permits monitoring the flux reaction by measuring the rate of evolution of SO_2.

2) The second peak in the plot of sulphur dioxide concentration is dirctly related to the quality of the flux contained in the sample. A flux quality parameter (FQP) has been defined as the height to time ratio of the second peak.

3) With regards to melting point and free silica of a flux mixture, free silica content has a much stronger impact on the flux quality.

4) Under the experimental conditions outlined previously, silica was found to be responsible for 60% of the sulphur dioxide evolved.

5) For pure silica flux, the flux quality reaches a limiting value of 5094 ppm/min at a particle diameter of 0.1 mm.

6) Minerals in the flux that do contain silica (other than quartz) affect the flux quality to a greater extent than non-silica containing minerals.

7) Of the silica containing minerals found in several industrial fluxes, feldspar and chlorite were found to diminish the flux quality, whereas mica was found to have little effect.

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